

IDNR Ambient Groundwater Quality Monitoring Summary for Fiscal Year 2016

Annual collection of groundwater monitoring data is important for assessing the quality of water in Iowa's major aquifers, which may be used for a wide variety of purposes including drinking-water for humans and livestock, irrigation, and industrial activities. Groundwater discharges to surface-water can also contribute significantly to surface-water quality, especially during periods of low rainfall. While public drinking water supplies are required to test for contaminants in finished water, the Iowa Department of Natural Resources' (IDNR) ambient groundwater quality monitoring program focuses on raw (untreated) water, most of which is collected from individual public water supply wells. Results of these analyses help us to understand what contaminants are present and how their concentrations change over time. The ambient groundwater quality monitoring efforts in fiscal years (FY) 2015 and 2016 targeted wells considered to be vulnerable to surface activities. A summary of FY 2015's monitoring can be found in the 2015 issue of IGWA UnderGround. The following is a summary of results from FY 2016.

From October 2015 to March 2016, untreated groundwater samples were collected from 68 public water supply wells in Iowa (see Figure 1). Half (34) of the sampled wells are located in alluvial aquifers with less than 40 feet of confining materials. The other 34 wells represent buried sand-and-gravel and bedrock aquifers with less than 130 feet of confining materials. Most of the wells (76%) were sampled in the fall (October – December), 21% of samples were collected in winter (January – March), and 2 samples (3%) were collected in early April. Water samples were analyzed for basic water quality parameters (total suspended solids, total dissolved solids, carbonate and bicarbonate alkalinity), chloride, nutrients (total Kjeldahl nitrogen, ammonia as nitrogen, nitrate + nitrite as nitrogen, total phosphorus, and orthophosphate as phosphorus), atrazine and its degradates (desethyl atrazine, deisopropyl atrazine, and desethyl-deisopropyl atrazine), and chloroacetanilide herbicides (alachlor, acetochlor, dimethenamid, metolachlor) and their ethanesulfonic acid (ESA) and oxanilic acid (OXA) degradates). In addition, a subset of these samples were analyzed for radionuclides as part of a graduate student research project. Results of general water quality, nutrient, and herbicide analyses for FY2016 are summarized in Table 1. Overall, results from the FY2016 monitoring season were very similar to FY2015, which represented a similar set of wells considered vulnerable to surface contamination based on confining layer thickness.

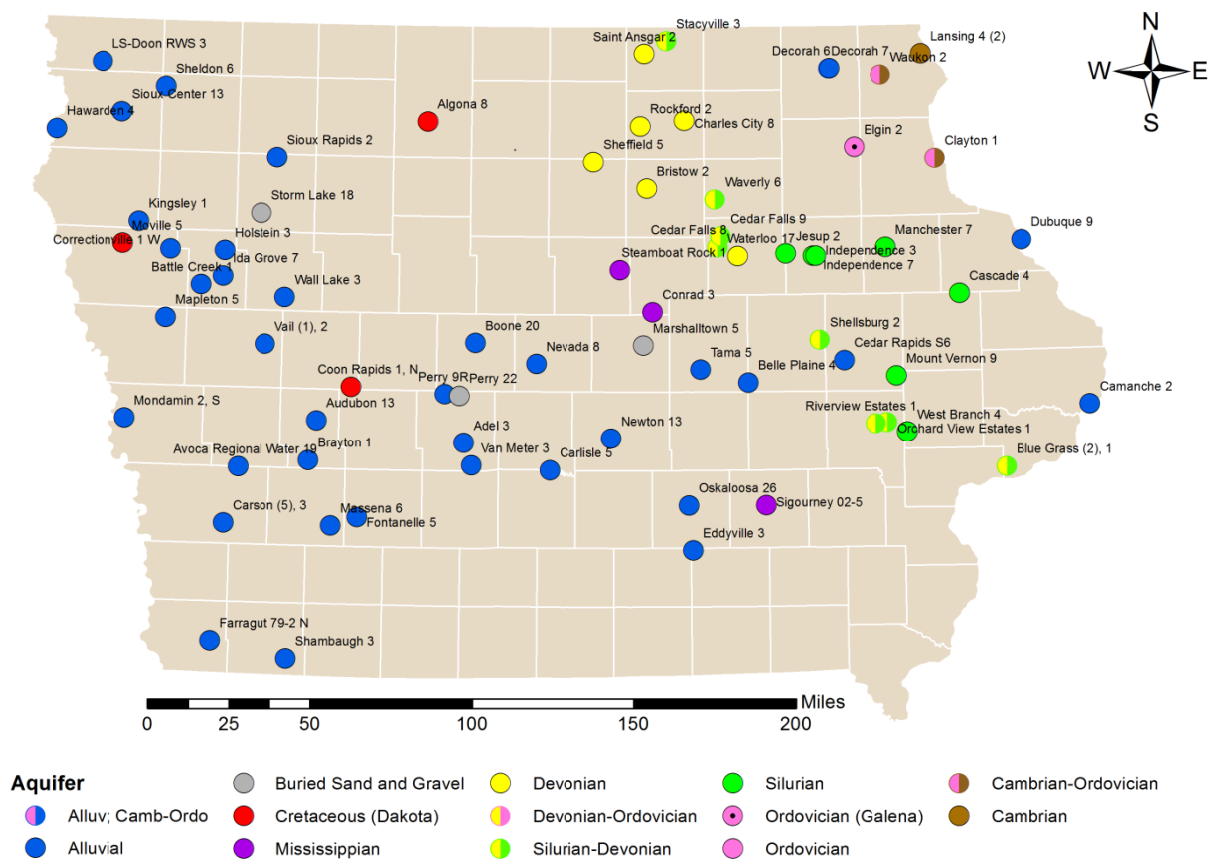


Figure 1. Ambient groundwater quality monitoring sites for FY2016 by aquifer.

Table 1. Summary statistics for general water quality parameters, nutrients, and herbicides.

Group	Analyte	Limit of Detection	Method	N	Number of Detections	Percent Detections	Mean of Detections	Median of all values*	Maximum
General Water Quality	Total Dissolved Solids	1 mg/L	SM2540 C	68	68	100%	440	410	760
	Total Suspended Solids	1 mg/L	USGS I-3765-85	68	25	37%	6	ND	30
	Bicarbonate Alkalinity	1 mg/L	SM 2320 B	68	68	100%	281	270	500
	Carbonate Alkalinity	1 mg/L	SM 2320 B	68	0	0%	ND	ND	ND
	Chloride	1 mg/L	EPA 300.0	68	64.0	94%	29	20	150
Nutrients	Nitrate + Nitrite nitrogen as N	0.1 mg/L	LAC 10-107-04-1J	68	41	60%	5.9	1.8	24
	Ammonia Nitrogen as N	0.05 mg/L	LAC 10-107-06-1J	68	25	37%	0.50	ND	2.00
	Total Kjeldahl Nitrogen as N	0.1 mg/L	LAC 10-107-06-2E	68	24	35%	0.5	ND	1.7
	Total Phosphorus as P	0.02 mg/L	LAC 10-115-01-1D	68	66	97%	0.11	0.07	0.68
	Ortho-Phosphate as P	0.02 mg/L	LAC 10-115-01-1A	68	29	43%	0.06	ND	0.14
Herbicides and Degradates	Atrazine	0.020 µg/L	EPA 536	68	18	26%	0.060	ND	0.290
	Desethyl Atz.	0.020 µg/L	EPA 536	68	19	28%	0.059	ND	0.170
	Desisopropyl Atz.	0.020 µg/L	EPA 536	68	0	0%	ND	ND	ND
	Desethyl-Deisopropyl Atz.	0.020 µg/L	EPA 536	62	22	35%	0.109	ND	0.32
	Acetochlor	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	2	3%	0.042	ND	0.055
	Acetochlor ESA	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	29	43%	0.276	ND	1.100
	Acetochlor OXA	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	16	24%	0.537	ND	<0.025
	Alachlor	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	0	0%	ND	ND	0.030
	Alachlor ESA	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	36	53%	0.223	0.037	0.950
	Alachlor OXA	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	8	12%	0.601	ND	4.100
	Dimethenamid	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	1	1%	ND	ND	0.057
	Dimethenamid ESA	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	4	6%	0.038	ND	0.046
	Dimethenamid OXA	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	3	4%	0.051	ND	0.077
	Metolachlor	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	8	12%	0.408	ND	1.600
	Metolachlor ESA	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	53	78%	0.505	0.225	4.000
	Metolachlor OXA	0.025 µg/L	SOP UHL-H-016 LC/MS/MS	68	24	35%	0.619	ND	7.100

*Includes non-detections

Nitrate and nitrite contamination of groundwater supplies has been an ongoing concern for over 30 years. While the primary concerns are related to acute toxicity for babies under 6-months of age and for pregnant woman with certain metabolic diseases, recent studies have also shown that chronic exposures to elevated nitrate in drinking-water and diet is a potential risk-factor for certain types of cancers. One recently published study looked at 34,708 post-menopausal women in Iowa and found that women who consumed drinking water with greater than 5 mg/L nitrate as N for four or more years had significantly greater incidence of bladder cancer than those with no comparable nitrate exposure.¹ In FY2016, nitrate + nitrite as nitrogen (N) was detected in 60% of the wells, with a median concentration of 1.8 mg/L, and a maximum concentration of 24 mg/L. Six wells had nitrate + nitrite as N concentrations above the Environmental Protection Agency's (EPA's) maximum contaminant level (MCL) of 10 mg/L nitrate in drinking-water (the MCL for nitrite as N is 1 mg/L). The highest nitrate + nitrite concentrations were found in alluvial wells in northwest Iowa and in one Devonian well in north-central Iowa (Figure 2). It should be noted that all of the public water supplies that participated in this study were compliant with both nitrate and nitrite standards in their finished water in 2015.² It should also be noted that while nitrate concentrations are generally lower in the winter in shallow groundwater, warmer than average soil temperatures and significant rainfall in the fall of 2016 may have raised nitrate + nitrite concentrations above typical levels for this time of year in some locations.

Ammonia as N was detected in 37% of the wells. Twenty-four of the 25 detections of ammonia occurred in wells where nitrate was not detected. While there is no MCL for ammonia in drinking water, the presence of ammonia at or above 1.0 mg/L indicates a potential for exceeding the nitrite MCL of 1.0 mg/L. The presence of ammonia enhances the formation of chloramines and can cause drinking water systems to feed more chlorine to ensure sufficient disinfection. Only three wells (4%) contained ammonia above 1.0 mg/L. The maximum concentration (2 mg/L) occurred in a well that draws water from a buried sand and gravel aquifer with an estimated confining layer thickness of 116 feet, indicating that the ammonia was likely derived from aquifer materials, and not from a surface source.

Phosphorus is not a concern for drinking-water, but along with nitrogen, it can contribute to the growth of algae in surface waters. In Minnesota, draft nutrient criteria for streams limit total phosphorus (TP) to between 0.050 – 0.150 mg/L depending on the ecoregion.³ In FY2016, 25% of the Iowa groundwater samples exceeded 0.150 mg/L. Ranges of TP and orthophosphate as P (PO₄-P) concentrations by aquifer type are shown in Figure 3. The majority of these relatively high TP concentrations occurred in alluvial samples, including the three highest concentrations: 0.42 mg/L in Missouri River alluvium, 0.51 mg/L in Mississippi River alluvium, and 0.68 mg/L in West Fork Middle Nodaway River alluvium. Similarly, PO₄-P concentrations were highest in alluvial aquifers, with a median PO₄-P concentration of 0.035 mg/L, and a maximum concentration of 0.14 mg/L. Both TP and PO₄-P

concentrations were significantly lower in bedrock aquifers: 90% of the samples from bedrock aquifers contained less than 0.100 mg/L TP and 75% of bedrock samples had no detectable orthophosphate. The three samples taken from buried sand and gravel aquifers ranged from 0.100 to 0.280 mg/L TP, none of which contained detectable levels of orthophosphate.

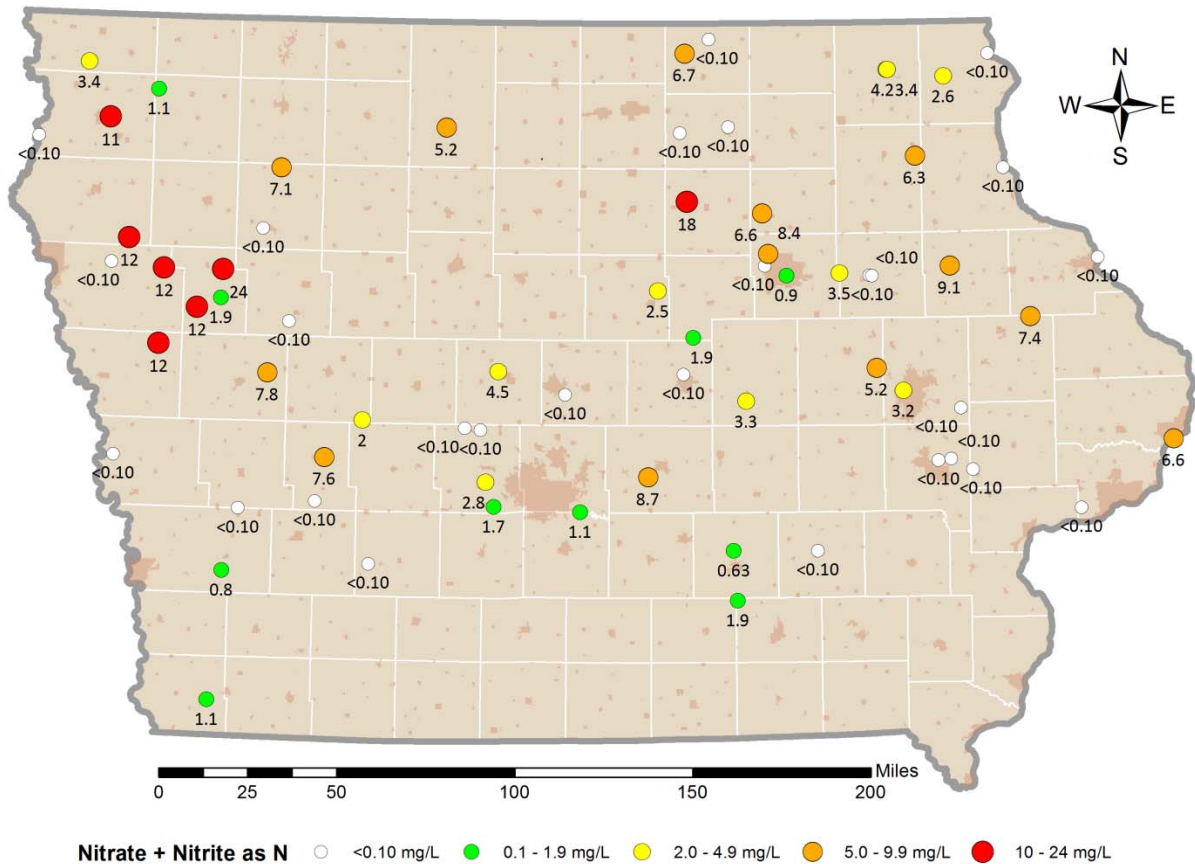


Figure 2. Concentrations of nitrate + nitrite as nitrogen (N) in untreated groundwater samples (FY2016).

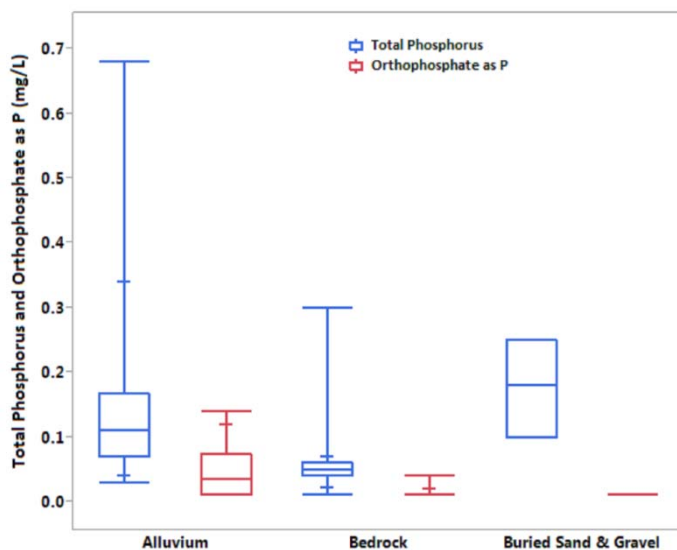


Figure 3. Quantile boxplots showing ranges of total phosphorus and orthophosphate as P concentrations by aquifer type.

Atrazine is a commonly used herbicide in Iowa.⁴ At sufficient concentrations, atrazine has been shown to disrupt the estrous cycles of rats and cause feminization of certain species of frogs. Atrazine was detected at low levels (maximum concentration of 0.240 µg/L or ppb) in 26% of the wells. These concentrations are well below EPA's MCL for in drinking-water of 3 µg/L atrazine. The chloro-s-triazine degradates of atrazine are thought to have similar toxicological effects. In FY2016, two of the three measured degradates of atrazine were detected: desethyl atrazine in 28% of samples, and desethyl-deisopropyl atrazine (also known as 2-chloro-4,6-diamino-s-triazine, or diamino atrazine) in 35% of samples. It appears that the timing of sampling may have had an effect on concentrations of desethyl atrazine and desethyl-deisopropyl atrazine as illustrated in Figure 4. The maximum combined concentration of atrazine and its three degradates was 0.38 µg/L, which is also well below EPA's MCL, and is far below the World Health Organization's drinking-water guideline for atrazine and its chloro-s-triazine degradates of 100 µg/L.

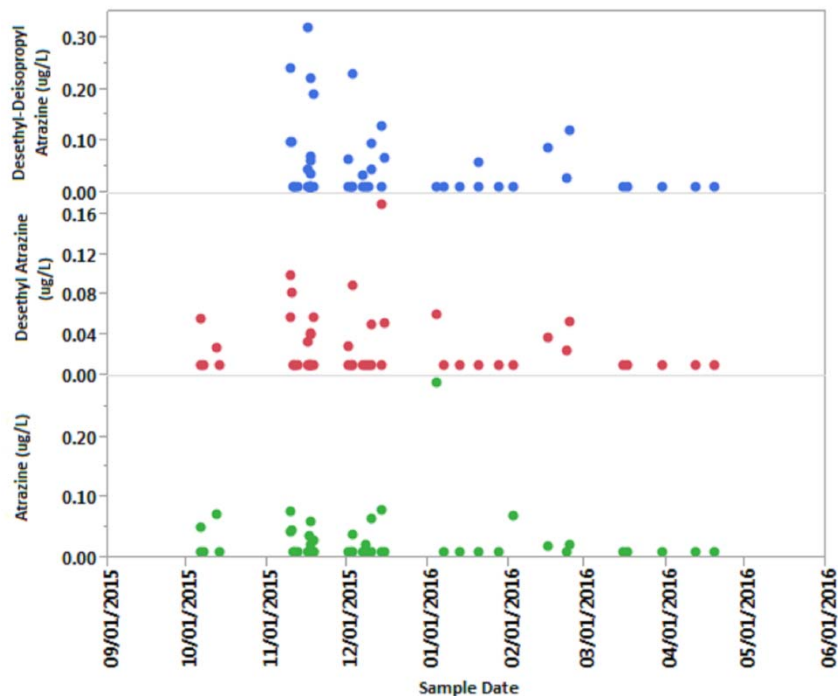


Figure 4. Concentrations of atrazine and its degradates over time.

Among the chloroacetanilide herbicides tested, EPA has only set a drinking-water standard for alachlor (2 µg/L), which was not detected in this study. The remaining chloroacetanilides that were tested are not currently subject to drinking water regulations, but alachlor ESA and OXA, acetochlor and its degradates, and metolachlor and its degradates are listed on the EPA's Contaminant Candidate List indicating that additional investigation of the public health risks associated with these compounds is a priority. Concentrations of metolachlor were below the World Health Organization's recommended guideline for drinking-water of 10 µg/L. The most commonly detected herbicide compound was the

degrade, metolachlor ESA, which was present in 78% of the samples at concentrations up to 4.0 µg/L with a median of 0.225 µg/L. The highest measured concentration of an herbicide was 7.1 µg/L of the degrade metolachlor OXA. Concentrations of metolachlor ESA (Figure 5) and the other chloroacetanilide herbicides were generally highest in Silurian or Silurian-Devonian wells in east-central Iowa. Timing of sampling appears to have had the greatest effect on alachlor ESA concentrations, which were higher in November and December than in other months, although the differences between months were not statistically significant. Most (97%) of the cumulative concentrations of herbicides (including atrazine, the chloroacetanilides, and their degradates) in the wells tested were below 3 µg/L; the remaining two wells had total herbicide concentrations of 11.8 and 19.1 µg/L.

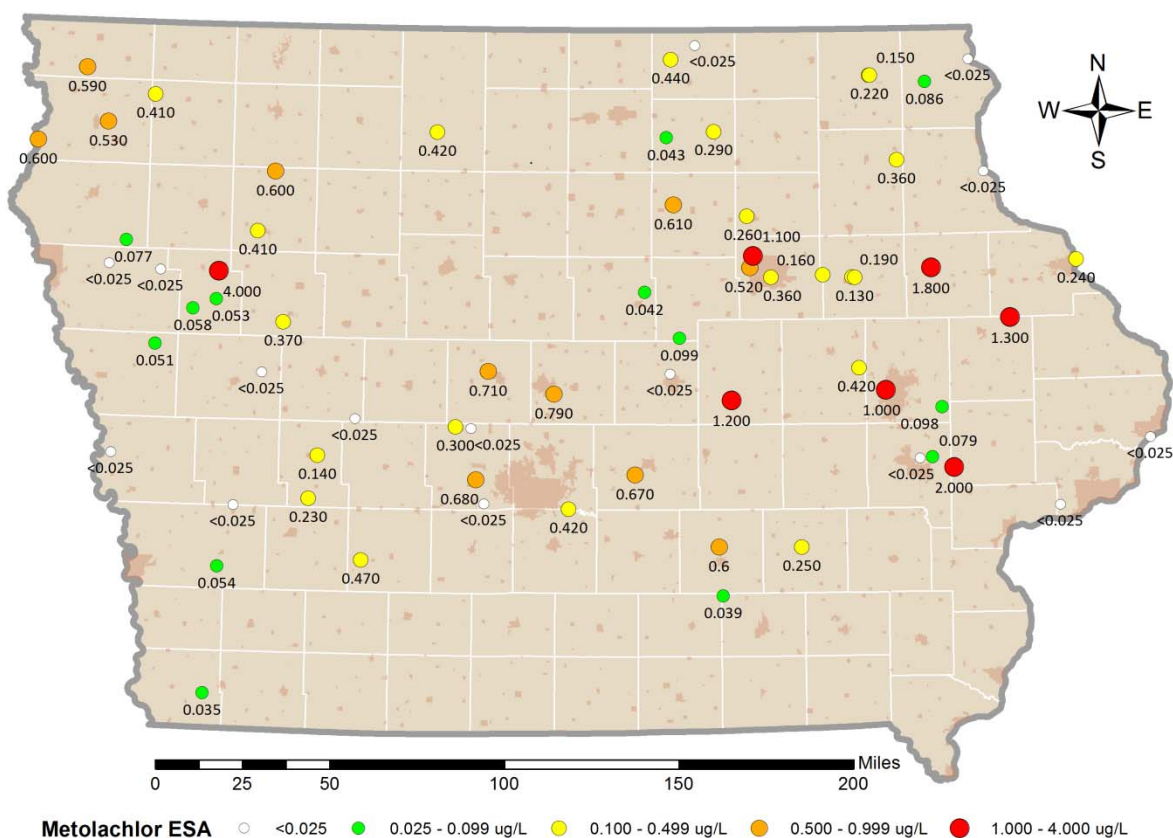


Figure 5. Concentrations of metolachlor ESA in untreated groundwater samples (FY2016).

This is the third consecutive year that untreated groundwater from public wells in Iowa has been tested for atrazine, the chloroacetanilide herbicides, and their degradates. No statistically significant differences in the distributions of concentrations of these compounds are seen between years (2013-2016) when grouped by aquifer. The lack of significance may result from small sample sizes and low detection frequencies. Further examination of data from individual wells may reveal more information about changes in concentration from year to year.

Monitoring of herbicide concentrations in Iowa's groundwater also took place in the 1990's and early 2000's. Although a thorough statistical analysis has not yet been completed, it appears that wells that contained measurable levels of atrazine and metolachlor in 2001-2004 often contain the same compounds in 2013-2016, but at lower concentrations. Most of the samples from the 2001-2004 period were collected in July and August, while the 2013-2016 samples were collected between October and March; therefore, it is possible that some of the differences between these sample sets result from seasonal variations in herbicide concentrations relating to the timing of application. Continued monitoring of these and other agricultural chemicals in groundwater is necessary as use of these chemicals changes over time. Use of alachlor has been dropping since the 1990's and sales are no longer allowed in the U.S. as of this summer.⁵ Meanwhile, the use of a new formulation of metolachlor (metolachlor-S) is increasing, and the use of acetochlor and atrazine on corn has remained relatively consistent for two decades.⁴

Public drinking water supplies are required to test quarterly for radionuclides in finished water, and the drinking-water standards apply to average values of four quarterly samples, thus, these data are not helpful for characterizing radionuclide concentrations in raw groundwater. In cooperation with the State Hygienic Laboratory, Dustin May analyzed untreated groundwater from 52 of the public wells sampled in FY2016 for radionuclides including gross alpha (including uranium) radioactivity, gross beta radioactivity, and radium-226. While the majority (90%) of samples had gross alpha (including uranium) levels below 6 picocuries per liter (pCi/L), four communities in western Iowa contained gross alpha levels above 10 pCi/L (two in alluvial wells, and two in Dakota wells) (Figure 6). All samples were below Iowa's drinking-water MCL for gross alpha radioactivity (excluding uranium) of 15 pCi/L.

References cited:

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- 4 - Pesticide National Synthesis Project website published by the National Water-Quality Assessment Program of the United States Geological Survey: https://water.usgs.gov/nawqa/pnsp/usage/maps/compound_listing.php
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